CA2048715

Publication Title:

POLYAMIDE FUEL LINES HAVING A GLASS FIBER REINFORCED MIDDLE LAYER

Abstract:

A cold impact resistant polyamide fuel line for motor vehicles which is stable in length, which can be briefly thermally overloaded, and which consists of at least three layers of mutually compatible polyamides. The polyamide fuel line according to the invention preferably also has an internal layer and an external layer of impact strength-modified polyamide with or without a plasticizer, and a glass fiber-reinforced layer in the middle of the pipe wall of impact modifier-free or impact-modified homopolyamide, copolyamide or blends thereof.

Consommation
et Corporations Canada

Bureau des brevets

Ottawa, Canada
K1A 0C9

Consumer and
Corporate Affairs Canada

Patent Office

(21) (A1) 2,048,715

(22) 1991/08/08

(43) 1992/02/10

5,009,8/81

(51) INTL.CL. ^{5} F16L-011/08; B32B-027/34; B32B-001/08

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Polyamide Fuel Lines Having a Glass Fiber Reinforced Middle Layer

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(30) (DE) DE 40 25 300.7 1990/08/09

(57) 19 Claims

Notice: The specification contained herein as filed

Abstract of Disclosure

A cold impact resistant polyamide fuel line for motor vehicles which is stable in length, which can be briefly thermally overloaded, and which consists of at least three layers of mutually compatible polyamides. The polyamide fuel line according to the invention preferably also has an internal layer and an external layer of impact strength-modified polyamide with or without a plasticizer, and a glass fiber-reinforced layer in the middle of the pipe wall of impact modifier-free or impact-modified homopolyamide, copolyamide or blends thereof.

Polyamide Fuel Lines Having a Glass Fiber Reinforced Middle Layer

This Application claims the benefit of the priority of German 40 25 300.7, filed August 9, 1990.

This invention relates to a cold impact resistant polyamide fuel line which is stable in length and can be briefly thermally loaded.

BACKGROUND OF THE INVENTION

Fuel lines, so-called mono-pipes consisting of a single homogeneous layer of polyamide 11 or 12, have been installed in motor vehicles for a long time. An essential disadvantage of such fuel lines resides in the considerable absorption capacity of the polymers for individual components of the fuels which leads to swelling and to changes of length in the walls and wall layers. Differing swelling in various wall parts is a particular problem.

A further disadvantage is that there is considerable permeation of conventional fuels through the walls of such mono-pipes which is unreasonably high in view of the environmental and safety considerations which have arisen in recent years and have to be taken into consideration.

Developments have therefore been made in order to improve such mono-pipes. One possibility consists in replacement by multi-layered pipes fabricated of polymers of the same or different types.

A fuel line is known from DE 35 10 395 A1 in which ethylene/vinyl alcohol copolymers are laminated to polyamide 11 or 12 layers. However, the adhesion between these layers is so low that they delaminate easily. Also, corrosive chemicals such as scattered salt can penetrate between the layers at the delaminated pipe ends. Furthermore, the adhesion to fittings with mandrel profiles is markedly reduced. Moreover, the cold impact resistance of such pipes is so low that they cannot withstand cold impact tests according to ISO 7628, DIN 73 378, and SAE J 4844d, because of the extremely brittle polyethylene vinyl alcohol layer used as the inner wall. The three-layer-tube as claimed in DE 38 21 723 is made from polyamide with a polyolefin middle layer and shows, besides low-stability in length, a limited stability under elevated temperatures due to its polyolefin component.

In addition, DE 38 27 092 describes a fuel line in which thermoplastic polyester elastomers are laminated to polyamide 6 and to a polyethylene vinyl alcohol internal layer. As in the previously discussed case, only slight adhesion exists between the layers so that the above-described disadvantages arise here as well.

SUMMARY OF THE INVENTION

It is therefore an object of the invention to provide a polyamide fuel line, which is stable in length, which exhibits sufficient resistance to permeation by all conventional fuels for current environmental and safety regulations without having the above-mentioned disadvantages.

To achieve this object, there is provided a cold impact resistant polyamide pipeline, which is not only stable in length, but also can be briefly thermally overloaded. It consists of at least three layers of mutually compatible polyamide polymers, wherein at least one layer is reinforced with glass fibers.

The invention will be described in connection with a fuel line for a motor vehicle, but its application is by no means so limited. The fuel line according to the invention has a permeation barrier which is adequate for current environmental and safety regulations, is delamination-free, and can be briefly overloaded at the temperatures usually occurring in the engine chamber of motor vehicles. Moreover, it is inexpensive to produce.

Known mono-pipes cannot withstand the bursting pressure test at 170°C. On the other hand, the multi-layered fuel lines according to the invention withstand a bursting pressure of 7 bar even at 180°C for a

short time, i.e. 1 to 2 hours. This is of considerable importance for the safety of fuel lines in cases where the engine overheats briefly, for example if the cooling system begins to malfunction.

Surprisingly, it has been found that the stability in length of a multi-layered polyamide pipeline is very high if at least one of the polymer layers is reinforced, for example with glass fibers. The high stability in length is also achieved if only one layer is reinforced. It has been found that this can be achieved preferably by reinforcing the relatively thin middle layer with glass fibers and can be improved by introducing impact strength modifiers into the middle layer. This combination also ensures good elongation at break behavior.

It has similarly been found that the following modified or unmodified polyamide types, which may contain plasticizers, are suitable as pipe layer materials: polyamide 11; 12; 12,12; 6; 6,6; polyamide elastomers based on polyamide 12; and partially aromatic polyamides. The three last-mentioned polyamides surpass the first-mentioned in their barrier effect against the aromatic, usually toxic constituents of fuels and are, therefore,particularly preferred for use as barrier layers in fuel lines.

A glass fiber-reinforced, impact-modified or impact modifier-free polyamide is compatible with the same

type of impact-modified but unreinforced polyamide. The same applies to other layer material combinations such as polyamide 6,6 with polyamide 6 on the one hand and polyamide 11 or 12 on the other hand, as well as polyamide 6,6 with blends of copolyamides and polyamide elastomers. It is preferred to use polyether esteramides based on the monomers of polyamide 11 or 12; the copolyamides of the monomers with 6, 11 or 12 carbon atoms are particularly suitable for the above-mentioned blends. No delamination could be observed on the pipelines from such polyamide layers.

According to the invention, therefore, multi-layered polyamide pipelines are provided, the external layer of which consists of impact-modified polyamides which may contain plasticizers and of which the glass fiber-reinforced middle layer consists of impact-modifier-free or impact-modified polyamide, preferably of polyamide 6, polyamide 12, or polyamide 6,6. The glass fiber-reinforced middle layer of such pipelines preferably consists of polyamide 6 or 12 which can also contain impact-modifiers.

Functionalized homopolyolefins or copolyolefins are used as impact-modifiers. These modifiers are present in amounts of 5% to 30% by weight and the glass fibers constitute 15% to 50% by weight. The ratio of the two additives is not critical and can be varied according to the requirements of the specific applications.

Combinations which consist internally and externally of impact-modified polyamide 6 or impact-modified polyamide 12 are preferred. A further preferred embodiment has roughly the same layer thickness in the internal and external layers, which is between 0.2 and 1.0 mm in practice. Thicknesses of 5% to 25% of the total wall thickness are sufficient for the glass fiber-reinforced middle layers. Thicknesses of 0.1 to 0.5 mm are, therefore, particularly preferred for the glass fiber-reinforced middle layer.

The polyamide pipelines according to the invention can obviously be made up from more than three layers if the principle of an impact-modified external layer and at least one reinforced layer, preferably between the internal and external layers is respected and the compatibility of the layer materials is ensured.

The multi-layered polyamide pipelines according to the invention are preferably produced by combining streams of melt in a coextrusion device. Such coextruded polyamide pipelines according to the invention have been tested with respect to their cold impact strength according to SAE J 844d, DIN 73 378, and ISO 7628, with respect to fuel permeation, and with respect to their stability in length.

The results of the cold impact tests are reproduced in Table 1. They have been carried out on pipes having an external diameter of 8 mm a wall thickness of 1 mm, and the layer structures are also indicated in the same Table. The polyamides mentioned are:

GRILON	XE3139	an impact-modified PA 6
GRILAMID	XE3148	an impact-modified PA 12 with plasticizer
GRILON	PVZ 3H	an impact-modified PA 6 with 30% glass fiber
GRILAMID	LV5 H	an impact-modifier-free PA 12 with 50% glass fiber

The above-mentioned polyamides are produced by EMS-CHEMIE AG, Zurich, Switzerland. The same applies to

GRILON	T300 GM	an impact-modifier-free PA 66
GRILAMID	ELY20NZ	an impact-modified polyamide elastomer
GRILON	CA6E	an amorphous copolyamide based on caprolactam/laurolactam

GRILON	R47HW	a high-viscosity, impact-modified PA 6 with a defined plasticizer content
GRILAMID	L25W20	a polyamide 12 with a defined plasticizer content
GRILAMID	L25W40	a polyamide 12 with a defined (higher) plasticizer content

which have additionally been used for comparison tests according to Table 1 and Figures 2 to 5.

In the accompanying drawings, constituting a part hereof and in which like reference characters indicate like parts,

Figure 1	is a diagrammatic view of a permeability testing device;
Figures 2-4	are bar graphs indicating the permeability of various polyamide resins to various fuels; and
Figure 5	is a graph similar to Figures 2-4 showing permeability at different temperatures.

The apparatus used for the permeation tests is shown in Figure 1. The fuel flows in fuel circuit 1 which contains an air chamber 3 and passes through heater 4 and a portion of pipe 5 of a pipeline to be tested. Pressure tank 2 communicates with the air chamber 3 and serves to maintain a pressure of 4 bar in fuel circuit 1. The fuel flows in the fuel circuit 1 at about 10 liters/h and is heated to 70°C by heater 4.

The apparatus also includes carrier circuit 6 which is connected to both ends of pipe 5. Carrier circuit 6 also has array 7 of activated carbon filters. The fuel which has permeated through the wall of pipe 5 is conveyed in carrier circuit 6 with 100 ml/min of nitrogen over activated carbon filter array 7, and its weight after 300 hours is determined. Like the impact measurements, these permeation tests were carried out on pipes having an external diameter of 8 mm and a wall thickness of 1 mm.

The length stability of the pipes according to the invention was determined by measuring the change in length of pipeline portions having an external diameter of 8 mm and a wall thickness of 1 mm while fuel flowed therethrough for 300 hours in an apparatus similar to the permeation apparatus of Figure 1.

The results of the length stability tests are to be found in Table 1. The results of the permeation tests are reproduced in Figures 2 to 4, while Figure 5 relates to the analysis of aromatic substances.

FAM is a blend of 50% toluol, 30% isooctane, 15% isobutene, 5% ethanol.

FAM 15 in Figure 5 is a blend of 84,5% FAM, 0,5% water, and 15% methanol.

Table 1: Cold impact tests and changes of length of pipes having 8 mm external diameters and 1 mm total wall thicknesses with glass fibre-reinforced middle layers and of comparison pipes

Example	Layer structure			Change of Length	Cold impact with striking apparatus		
					SAE J844d	DIN 73 378	ISO 7628
1. Comparison example Middle layer not reinforced	Grilon EVAL F Grilon	XE3139 XE 3139	0.60 mm internal 0.10 mm middle 0.30 mm external	1.5%	Failed	Failed	Failed
2. Comparison example Middle layer not reinforced	Grilon Grilon Grilon	SE 3139 T 300GM XE 3139	0.45 mm internal 0.10 mm middle 0.45 mm external	3.0%	Successful	Successful	Successful
3. Comparison example Middle layer not reinforced	Grilon Grilamid Grilon Grilamid	XE 3139 ELY20NZ 50%) CA6E 50%) XE 3148	0.60 mm internal 0.20 mm middle 0.20 mm external	3.5%	Successful	Successful	Successful
4. Middle layer GF-reinforced	Grilon Grilon Grilon	XE 3139 PVZ 3H SE 3139	0.45 mm internal 0.10 mm middle 0.45 mm external	0.1%	Successful	Successful	Successful
5. Middle layer GF-reinforced	Grilamid Grilamid Grilamid	XE 3148 LV 5H XE 3148	0.45 mm internal 0.10 mm middle 0.45 mm external	0.1%	Successful	Successful	Successful

I CLAIM

1. A cold impact resistant pipeline comprising at least three component layers of mutually compatible polyamides, at least one of said component layers being reinforced by glass fibers, whereby said pipeline is stable in length, can be briefly thermally loaded, and is cold impact resistant.

2. The pipeline of Claim 1 wherein said glass fibers are in an intermediate layer located between at least two other layers.

3. The pipeline of Claim 1 wherein there are an internal layer, an external layer, and an intermediate layer between said internal layer and said external layer, said internal layer and said external layer being of impact-modified polyamide, said intermediate layer of homopolyamide, copolyamide or blends thereof and containing said glass fibers.

4. The pipeline of Claim 3 wherein said intermediate layer is selected from the group consisting of polyamide 6,6; polyamide 6; polyamide 11; polyamide 12; polyamide 12,12; and partially aromatic polyamide.

5. The pipeline of Claim 3 wherein said intermediate layer is of a blend of polyamide elastomers.

6. The pipeline of Claim 5 wherein said elastomers are a polyether esteramide or a copolyamide.

7. The pipeline of Claim 6 wherein said elastomers are derived from monomers having 6 to 12 carbon atoms.

8. The pipeline of Claim 1 wherein at least one of said component layers contains an impact-modifier.

9. The pipeline of Claim 8 wherein said at least one of said component layers contains 5% to 30% by weight of said impact modifier.

10. The pipeline of Claim 8 wherein said impact-modifier is a functionalized homopolyolefin or a functionalized copolyolefin.

11. The pipeline of Claim 1 wherein said component layer containing said glass fiber has 15% to 50% by weight of said glass fibers.

12. The pipeline of Claim 1 comprising an internal layer and an external layer, said internal layer and said external layer having about the same thickness.

13. The pipeline of Claim 12 wherein said thickness is 0.2 to 1.0 mm.

14. The pipeline of Claim 1 wherein said component layer containing said glass fibers has a wall thickness of about 5% to about 25% of the total thickness of said component layers.

15. The pipeline of Claim 14 wherein said wall thickness is 0.1 to 0.5 mm.

16. The pipeline of Claim 3 wherein said internal layer and said external layer are of impact-modified polyamide 12, and said intermediate layer is of polyamide 12 having no impact-modifier.

17. The pipeline of Claim 3 wherein said intermediate layer contains an impact-modifier.

18. The pipeline of Claim 17 wherein said internal layer, said intermediate layer, and said external layer comprise polyamide 6, and said intermediate layer is impact modified.

19. The pipeline of Claim 1, wherein at least one of said component layers contains plasticizer.

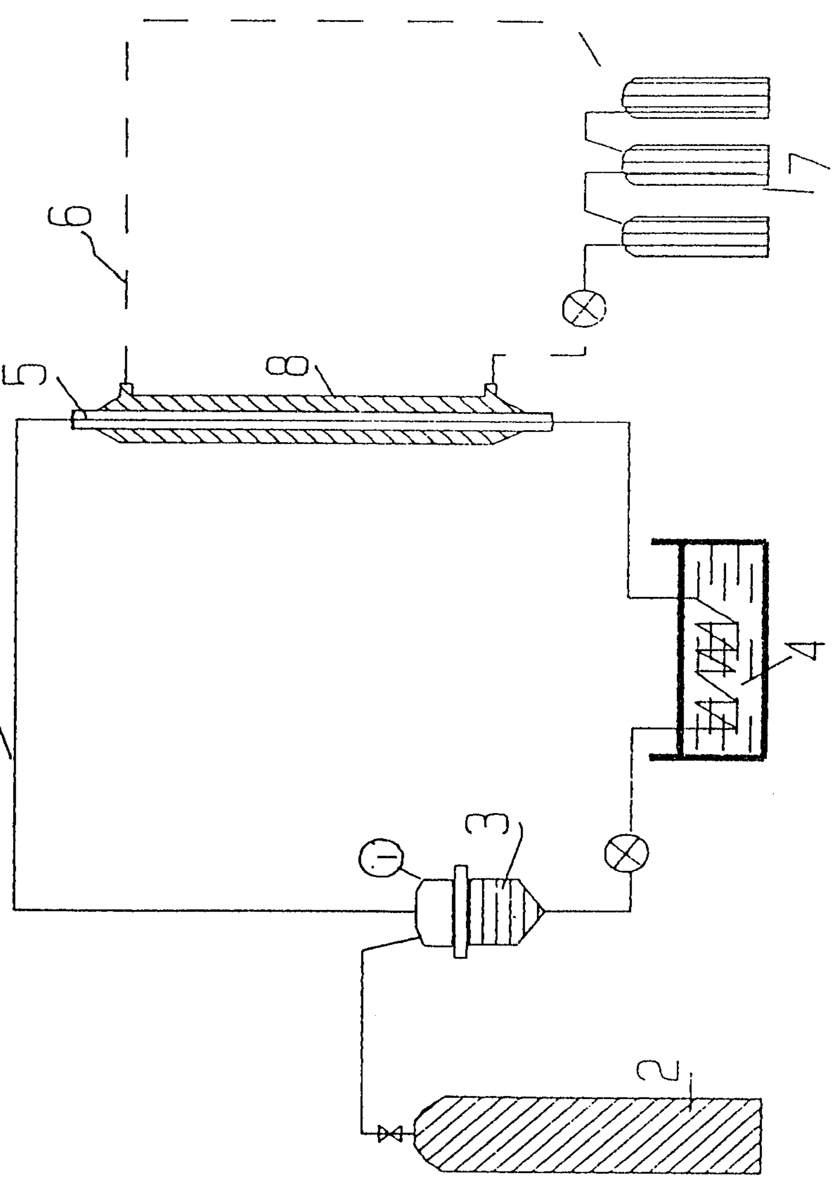

Figure 1

Alex E. MacRae & Co.

FUEL PERMEATION THROUGH PIPES 8 x 1 mm
T = 70°C 4 bar unleaded supergrade petrol
+ 5% ethanol, 3% methanol, 2% isopropanol

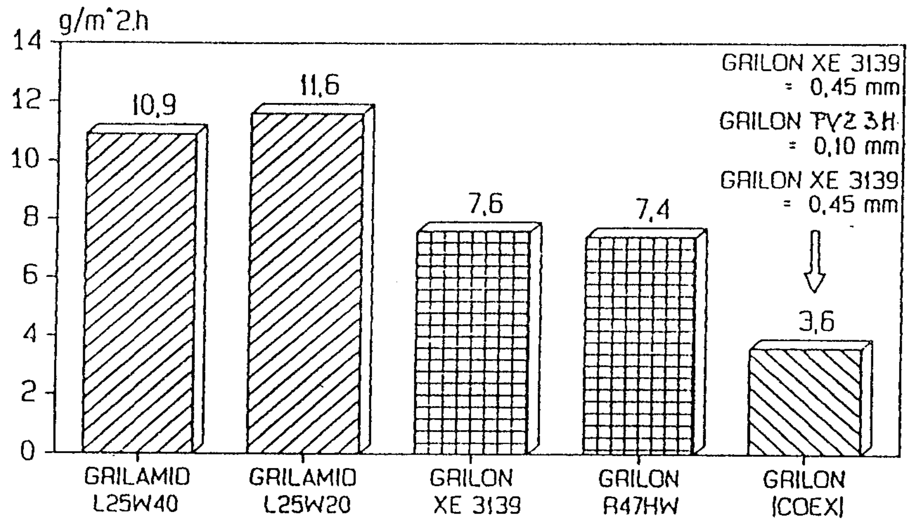

Figure 2

FUEL PERMEATION THROUGH PIPES 8 x 1 mm
T = 70°C 4 bar leaded supergrade petrol

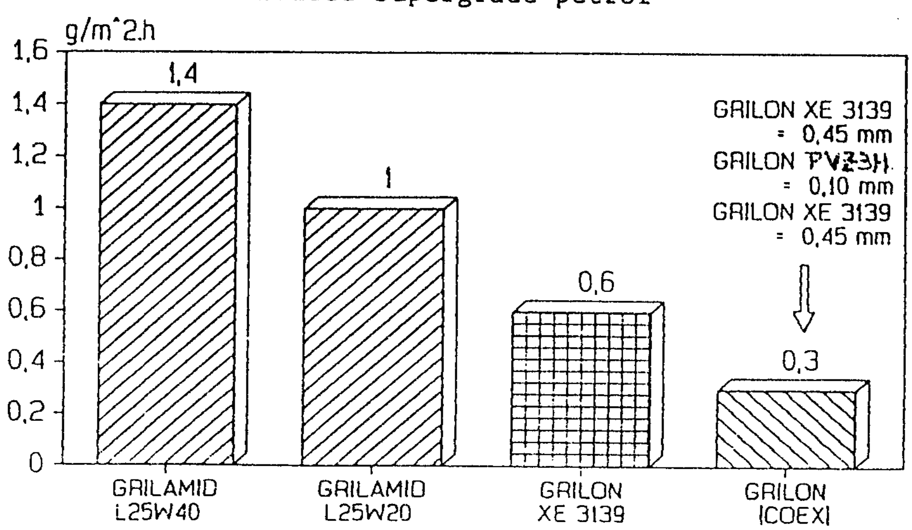

Figure 3

FUEL PERMEATION THROUGH PIPES 8 x 1 mm
T = 70° C 4 bar unleaded supergrade petrol

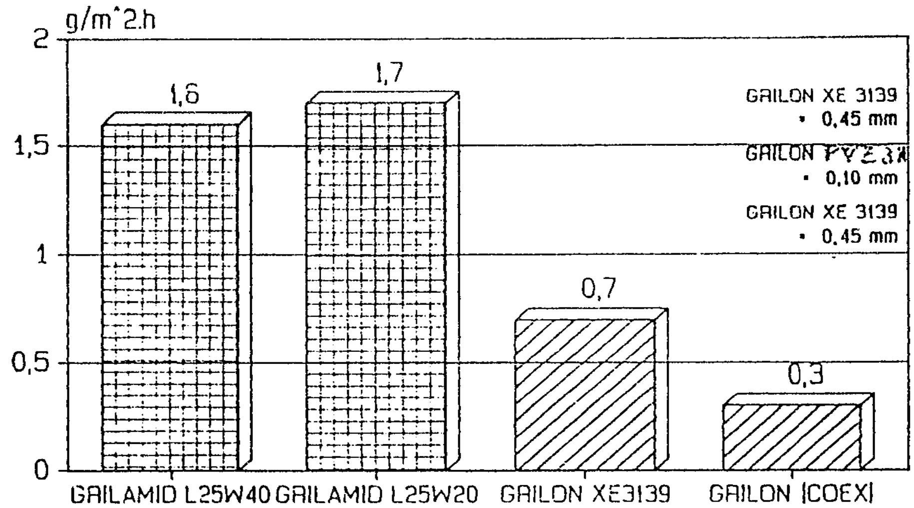

FIGURE 4

TOLUENE (AROMATIC CONSTITUENT) CONTENT IN
PERMEATED FAM 15
Initial toluene content in FAM 15 = 46.5%

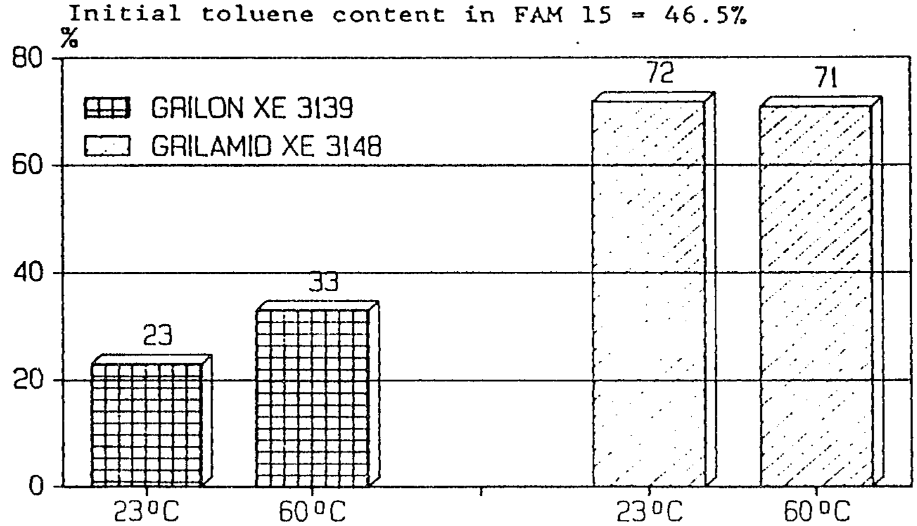

FIGURE 5

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